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Electrical and Optical Characterization of Silicon Carbide-Polytypes with Respect to High-Field Device Applications

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by

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Summary

The electrical properties of both shallow dopants (nitrogen (N), aluminum (Al) and boron (B)) and deep defect centers were investigated in silicon carbide (SiC) samples of various polytype using Hall effect, admittance spectroscopy and deep level transient spectroscopy (DLTS). SiC samples fabricated by the NASA-Lewis Research Center, Cleveland, Ohio were doped with N, Al or B during the epilayer growth and those fabricated by GE Corporate Research and Development were doped afterwards by B^+-implantation. The samples were provided by Dr. S. Saddow, Army Research Laboratory (ARL), Adelphi, Maryland.

With regard to the purpose of this project focusing on the suitability of SiC for high-field device applications, material properties like the degree of ionization of different shallow dopants (especially p-type dopants) at device operating temperatures, the possibility of impact ionization of intrinsic and extrinsic energetically deep defect centers as well as the high-field carrier mobility of both electrons and holes had to be considered.

It turns out that Al is the superior p-type dopant for SiC compared with B with respect to high-field applications for several reasons. At first, the Al ionization energy is about 100 meV lower than that of B, i.e. the degree of ionization of the Al acceptor level is higher than that one of B at room temperature. Furthermore, doping SiC with B leads to a compensating deep boron-related donor level; so far known, Al doesn't. This might limit the maximal applicable electric field in B-doped devices due to impact ionization of the deep boron-related donor termed D-center. In addition, Al is less diffusing compared with B. This fact is important for abrupt p-n junction devices, especially when fabricated by ion-implantation and subsequent annealing. Finally, the 4H-SiC NASA sample which was Al-doped during growth showed a remarkable high free hole Hall mobility, i.e. the high-field carrier mobility should be high as well.

List of Keywords

1. Introduction

Silicon carbide (SiC) is not only regarded as a promising semiconductor material for high-temperature and high-frequency, but also for high-field device applications [1, 2]. However, little is known about the influence of electrically active defect levels in the bandgap of SiC on its high-field performance. Theoretical calculations [1] so far neglected the impact ionization of partially ionized shallow and deep levels as there is a lack of experimental data on the ionization coefficients and their electrical field and temperature dependence of SiC polytypes in general.

Within the scope of this project, we characterized the properties of electrically active defects both shallow dopants like N, Al, B and deep defect centers in SiC samples fabricated either by the NASA-Lewis Research Center, Cleveland, Ohio or GE Corporate Research and Development by means of Hall effect, admittance spectroscopy and deep level transient spectroscopy (DLTS).

2. Impact ionization of defect centers

The maximal electric field applied on SiC devices is governed by the impact ionization rate α_n and α_p for electrons and holes, respectively.

Theoretical calculations [1] of SiC devices mostly considered impact ionization across the bandgap, where majority carriers with sufficient energy create additional electrons and holes. In SiC, however, the shallow n- and especially p-type dopants have a rather high ionization energy. Depending on the temperature, only a portion of the dopants is ionized. Hence, impact ionization of non-ionized donors or acceptors is possible creating additional electrons or holes. Deep defect centers can influence the impact ionization rates in the same way as shallow dopants leading to a charge carrier multiplication and subsequently to the avalanche breakdown.

The contribution of energetically shallow and deep defect centers to the impact ionization rate (per unit path length) α_n and α_p for electrons and holes, respectively, can be approximately described by [3]:

electrons:

$$\alpha_n = C \cdot \exp\left(-\frac{B \cdot (E_C - E_T)}{F^2}\right) \qquad (1a)$$

and holes:

$$\alpha_p = C \cdot \exp\left(-\frac{B \cdot (E_T - E_V)}{F^2}\right) \qquad (1b)$$

C: constant of the order of one

$$B \cong \frac{4\hbar \cdot \omega_{LO}}{e^2 \cdot \lambda^2}$$

ω_{LO}:   longitudinal optical phonon frequency
λ: carrier mean free path length
E_C: conduction band edge energy

E_V: valence band edge energy
E_T: ground level of the defect center
F: electric field strength.

From Eqs. (1a, b), one can see that the greater the ionization energy of the defect center ΔE_T ($\Delta E_T = E_C - E_T$ or $\Delta E_T = E_T - E_V$), the lower its contribution to the impact ionization rate α_n or α_p.

3. Carrier drift velocity and mobility of charge carriers

For high-field devices based on SiC, the carrier drift velocity $\vec{v}$ in the drift region (drift region: space charge region w excluding the avalanche region x_A, $x_A \leq x \leq w$; avalanche region: narrow region near the highest field, where most of the multiplication processes occur) of the device is an important parameter [4]. Minimizing the transit time of charge carriers in the drift region requires to achieve the saturation velocity v_s at the applied electric field. The relation between the carrier drift velocity $\vec{v}$ and the electric field $\vec{F}$ is given by

$$\vec{v} = \mu(F) \cdot \vec{F} \tag{2}$$

$\mu(F)$: field dependent mobility.

The experimental results for the electron saturation velocity $v_{s,n}$ in 6H-SiC obtained by v. Muench and Pettenpaul [5] were fitted with an exponential curve by Mehdi et al. [6] giving rise to the following equation for the field dependent mobility of electrons [1]:

$$\mu(F)_n = \frac{v_{s,n}}{F} \cdot \left(1 - \exp\left(-\frac{F \cdot \mu_n}{v_{s,n}} \right) \right) \tag{3}$$

μ_n: low-field drift mobility for electrons.

The field dependent mobility $\mu(F)$ and the low-field drift mobility μ, respectively (see eq. (3)), must, therefore, be high enough that the saturation velocity v_s can be reached at electric fields below avalanche breakdown due to impact ionization.

The low-field drift mobility μ can experimentally be expressed by the Hall mobility μ_H according to

$$\mu_H = r_H \cdot \mu \tag{4}$$

r_H: Hall scattering factor.

Hence, Hall effect measurements allow to estimate high-field mobility properties of charge carriers.

4. Degree of ionization of electrically active shallow dopants

The degree of ionization of a donor i in the bulk of SiC as a function of temperature is given by [1]

$$I_{D,i} = \frac{N_{D,i}^+}{N_{D,i}} = \frac{-1+\sqrt{1+4\cdot g_C\cdot\dfrac{N_{D,i}}{N_C}\cdot\exp\left(\dfrac{\Delta E_{D,i}}{kT}\right)}}{2\cdot g_C\cdot\dfrac{N_{D,i}}{N_C}\cdot\exp\left(\dfrac{\Delta E_{D,i}}{kT}\right)} \qquad (5)$$

g_C: degeneracy factor

$N_{D,i}$: concentration of donor i

N_C: effective density of states in the conduction band

$\Delta E_{D,i}$: ionization energy of donor i.

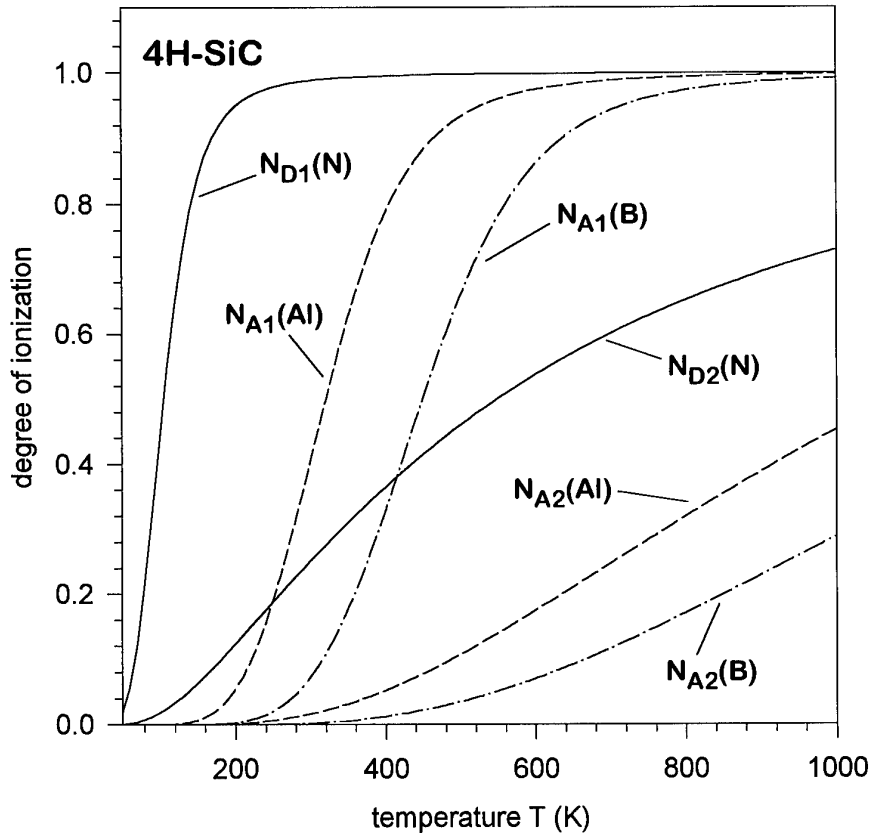A corresponding equation is valid for the degree of ionization of acceptors in SiC.

FIG. 1 Degree of ionization as a function of temperature for the shallow donor N (residing at hexagonal sites) and the acceptors Al and B in 4H-SiC for two different dopant concentrations.
Parmeters:
$\Delta E_D(N) = 50$ meV; $N_{D1}(N) = 1\cdot10^{16}$ cm^{-3}, $N_{D2}(N) = 1\cdot10^{19}$cm^{-3}
$\Delta E_A(Al) = 200$ meV; $N_{A1}(Al) = 1\cdot10^{16}$ cm^{-3}, $N_{A2}(Al) = 1\cdot10^{19}$cm^{-3}
$\Delta E_A(B) = 300$ meV; $N_{A1}(B) = 1\cdot10^{16}$ cm^{-3}, $N_{A2}(B) = 1\cdot10^{19}$cm^{-3}.

Fig. 1 shows the degree of ionization as a function of temperature for the shallow donor N (residing at hexagonal sites) and the acceptors Al and B in 4H-SiC for two different dopant concentrations. Due to their different ionization energies, the degree of ionization of these dopants differs strongly. We have determined the ionization energies of Al and B in the 4H-SiC NASA sample #1710-2 to be equal to 195 meV and 300 meV, respectively. This sample was doped with Al during the chemical vapor deposition (CVD) growth of the epilayer and was unintentionally contaminated with a high concentration of B probably by outdiffusion of B from the graphite material used in the CVD equipment. With respect to high-field device applications, the greater degree of ionization suggests Al to be the favorable p-type dopant for SiC since impact ionization of non-ionized acceptors is reduced for Al.

The situation for n-type doping looks more convenient as N has a rather low ionization energy of $E_N(h) = 52.1$ meV and $E_N(k) = 91.8$ meV in 4H-SiC (from infrared absorption measurements in Ref. [7]), respectively, for nitrogen donors residing at hexagonal (h) or at cubic (k) lattice sites. Correspondingly, the degree of ionization of n-type dopants is much higher at room temperature than that one of p-type dopants (see Fig. 1).

5. Hall mobility of p-type silicon carbide

As mentioned in section 3, the Hall mobility data allow to estimate the high-field mobility properties of charge carriers. In case the Hall mobility μ_H reaches high values, the field dependent mobility $\mu(F)$ is expected to do as well.

So far, high Hall mobility data have been reported for n-type 6H-SiC with $\mu_{H,n}(T=293K) = 400$ cm^2/Vs and $\mu_{H,n}$(max.) = 10000 cm^2/Vs at T = 45 K in the literature [8]; however, the highest values for p-type SiC only reach $\mu_{H,p}(T=293K) = 80$ cm^2/Vs and $\mu_{H,p}$(max.) = 240 cm^2/Vs at low temperatures [8].

The NASA p-type 4H-SiC epilayer #1710-2 grown by CVD showed remarkable high values for the hole Hall mobility of about 95 cm^2/Vs at room temperature and a maximum value of about 750 cm^2/Vs at T = 110 K.

There are no experimental results available for the hole saturation velocity $v_{s,p}$ by now. It is suggested that the breakdown electric field strength is too low to reach the hole saturation velocity [1]. Hence, an experimental expression for the field dependent mobility of holes comparable with that of electrons (section 3, Eq. (3)) is so far not known. Further effort is necessary to improve the quality of p-type SiC material in order to improve the Hall mobility of holes. Eliminating the boron contamination from the graphite and reducing the background concentration of nitrogen, should result in an improvement in NASA's CVD grown p-type SiC layers.

6. Energetically deep defect centers

Because of their influence on the impact ionization rates of electrons and holes, energetically deep defect centers were investigated in SiC samples fabricated by NASA-Lewis Research Center, Cleveland, Ohio and by GE Corporate Research and Development using deep level transient spectroscopy (DLTS). The provided p$^+$-n junction diodes were either doped with N

or Al (NASA) during the growth or by implantation of B^+ into an n-type epilayer forming a p^+-layer (GE Corporate Research and Development). In addition, the NASA samples allowed to compare the defect spectra of two different polytypes, because the epilayers were grown side by side with the 3C- and 6H-SiC polytype. The simultaneous formation of 3C- and 6H-SiC on the same 6H-SiC substrate was confirmed by identification of the shallow nitrogen donor from admittance spectroscopy data [9, 10].

A variety of minority and majority carrier levels was found in the DLTS spectra of NASA and GE SiC samples [9, 10, 11] discussed in the following.

In the 6H-SiC NASA diodes, a broad majority carrier peak with an ionization energy of about 700 meV with respect to the conduction band was observed; the simultaneously grown 3C-SiC diodes, however, revealed no majority carrier level in this energy range. The defect levels causing the broad DLTS peak in 6H-SiC spectra were discussed to be either of intrinsic nature like the Z_1/Z_2-center [8] or related to an impurity containing defect complex residing at the inequivalent cubic and hexagonal lattice sites. The experimental result that 3C-SiC doesn't show up with a corresponding defect center might be due to the fact that the ideal growth parameters are different for 3C- and 6H-SiC. With respect to deep defect centers, the applied growth conditions seem to be more adequate for 3C growth than for 6H.

Another broad majority carrier peak with an ionization energy of about 1 eV related to the conduction band was found in B^+-implanted GE diodes. Its chemical nature is so far unknown, however, it might be due to an individual deep defect center residing at the three inequivalent lattice sites (h, k_1, k_2) in the 6H polytype.

The minority carrier levels observed in the DLTS spectra of NASA's 3C- and 6H-SiC diodes were assigned to the boron-related D-center; an ionization energy of about 600 meV and 635 meV, respectively, related to the valence band could be evaluated for the two polytypes. The appearance of the D-center is reported after diffusion or implantation of B in 6H-SiC [12, 13] and after doping with B during CVD growth in 4H-SiC [14]. A microscopic model for the D-center has been presented in Ref. [13] suggesting that it consists of a complex of one B atom and one or more native defects, e.g. vacancies. Boron, therefore, is assumed to behave amphoteric: it can either reside at a silicon lattice site [15] giving rise to the "shallow" B acceptor level at about 300 meV above the valence band or at a carbon lattice site forming the deep boron-related D-center at about 620 meV above the valence band.

Recently Larkin et al. [16] reported investigations using the site-competition epitaxy to control the boron incorporation in CVD grown 6H-SiC epilayers. They demonstrated by secondary ion mass spectrometry (SIMS) analysis that an increase in B incorporation can be achieved by increasing the C/Si ratio either by decreasing the silane concentration or increasing the propane concentration during CVD growth. However, detailed electrical measurements have not been conducted on these CVD epilayers. Larkin et al. only stated the net acceptor concentration $N_A - N_D$ (N_A: acceptor concentration, N_D: donor concentration) determined from capacitance-voltage-(CV) measurements for two epilayers with different C/Si ratio (the boron concentration [B] was measured with SIMS) [16]:

C/Si	$(N_A - N_D)$/cm^{-3}	[B]/cm^{-3}	$\dfrac{N_A - N_D}{[B]}$
1.96	$5 \cdot 10^{15}$	$6.5 \cdot 10^{16}$	8 %
9.09	$3.5 \cdot 10^{17}$	$1 \cdot 10^{18}$	35 %

Larkin et al. infer from these results that B is preferentially occupying Si lattice sites leading to an increase of the "shallow" B acceptor. While the net acceptor concentration $N_A - N_D$

increased by a factor of 70 with growing C/Si ratio, the elemental boron concentration [B] only increased by a factor of 15. Probably the concentration of compensating donors N_D has changed, too, with increasing C/Si ratio. The compensation can vary with the nitrogen concentration and/or the concentration of the deep boron-related D-center. Kimoto et al. [17] reported a decreasing N incorporation with increasing C/Si ratio based on SIMS results. This result could explain that $(N_A - N_D)$ increases stronger than the boron concentration [B] in Larkin samples. In addition, the compensating influence of the D-center has to be considered; this is difficult to conduct on the basis of C-V measurements. In the literature, there are contradictory assertions about the charge state of the D-center: Ballandovich et al. [18] claim that it is acceptor-like; this statement is based on a comparison of defect concentrations observed by optically detected DLTS. Basically this measurement technique does not allow to make any statements on concentrations. Suttrop et al. [13] (6H-SiC) and Troffer et al. [14] (4H-SiC) infered from double correlated DLTS measurements that the D-center should be donor-like and, hence, contribute to the high compensation in B-doped samples. The latter is supported by results on 6H-SiC epilayers grown at our institute by liquid phase epitaxy (LPE) and doped with B during growth; these layers provide a high concentration of the D-center, but only a small one of the shallow B acceptor, they usually show n-type conductivity [19]. In case of the LPE growth, this is believed to be due to the growth condition, where carbon is diluted in a silicon melt; at typical growth temperatures, the content of silicon in the melt is about 4000 times higher than that one of carbon [19].

In contrast to the NASA samples, a D-center related minority carrier level could not be observed in the B^+-implanted GE diodes. This can be explained by the strong asymmetric p^+-n junction diodes fabricated by GE. While the difference of dopant concentration between the p^+- and the n-layer was about one order of magnitude in the NASA samples [9, 10], the n-layer in the GE diodes was overcompensated with boron by a factor of 250 in concentration [11]. Due to this asymmetry in doping, the space charge region of the p^+-n junction is mainly spread out in the n-layer, so that the sensitivity of the DLTS method for minority carrier levels in the GE diodes decreased extremely.

7. Conclusion

Considering the arguments given above, Al seems to be the superior p-type dopant for SiC compared with B with respect to high-field device applications.

The difference in the ionization energy between the Al acceptor and the shallow B acceptor leads to a remarkable higher degree of ionization of Al at any temperature (see Fig. 1). As impact ionization can only release trapped carriers from non-ionized acceptors, it is expected to be reduced for Al. However, a shallow acceptor with an even smaller ionization energy than Al would be desirable for SiC.

A second item is the contribution of energetically deep defect centers to the impact ionization rates and their influence on the avalanche breakdown in the space charge region of a SiC device. There is a major disadvantage of B compared with Al because of the deep boron-related D-center. No aluminum-related deep level similar to the D-center has been reported in the literature by now. As impact ionization of the D-center might lower the maximal applicable electric field in B-doped devices, Al seems to be the superior acceptor. In addition, we believe that the D-center is responsible for the high compensation in B-doped samples [14, 20].

A detailed SIMS analysis of B^+-implanted and subsequently annealed SiC epilayers revealed that B diffuses during the anneal into the undamaged bulk region and to the surface resulting

in a pile-up of the B concentration [20]. We also conducted comparable investigations on Al^+-implanted and annealed epilayers demonstrating a less pronounced diffusion of the Al acceptor [20]. The weak diffusion of Al is an important technological advantage of Al for the fabrication of more complex device structures using ion-implantation and subsequent annealing.

Finally we would like to point out that NASA's Al-doped 4H-SiC epilayer resulted in high hole Hall mobility values rising the hope that further improvements of the crystal quality should be possible to provide high-field carrier mobilities to reach the hole saturation velocity before avalanche breakdown takes place.

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